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Description

The invention relates to catalyst systems for the polymerization of olefins, the procatalyst of which comprises a solid carrier and a layer on its surface comprising a titanium compound, a magnesium compound and an electron donor. The invention also relates to the preparation of such a catalyst system and to the use of the catalyst system for the polymerization and copolymerization of alphaolefins.

For the polymerization of olefins is generally used a so-called Ziegler-Natta-catalyst system consisting of a so-called procatalyst and a cocatalyst. The procatalyst is based on a compound of a transition metal belonging to any of the groups IVB to VIII of the periodic table of elements and the cocatalyst is based on an organometallic compound of a metal belonging to any of the groups IA to IIIA of the periodic table. The catalyst system usually also comprises electron donors improving and modifying the catalytic properties.

In the preparation of heterogenic polymerization catalysts it is conventional to use as a component improving the polymerization activity of the procatalysts a carrier compound, on which the transition metal compound is layered. Common carrier compounds are silicon dioxide, aluminum oxide, magnesium oxide, titanium oxide, carbon in different forms, and different kinds of polymers. As important carrier compounds have proven magnesium compounds, such as alkoxides, hydroxides, hydroxyhalides and halides, of which the last-mentioned, especially magnesium dichloride, has lately grown to the most significant carrier component of the procatalyst compositions.

As magnesium halides do not in their basic crystal form become activated very efficiently by the transition metal compound, their crystal structure must be deformed. Conventionally this takes place by grinding e.g. in a ball mill, whereby finely-divided powder having typically a great specific area is obtained, the crystal lattice of which is greatly deformed. When such a powder is activated to a procatalyst composition by layering it with a transition metal compound and thereafter is reduced with a organometallic compound acting as a cocatalyst, a very active polymerization catalyst is obtained.

A drawback of the conventional grinding methods of magnesium halide is, however that they consume very much energy, cause wear and corrosion of the equipment and are suitable for the preparation of a catalyst by a laborious batch process only.

A newer and more efficient manner to decrease the crystallinity of magnesium halides and thus improve their ability to become activated by a transition metal compound, is to modify them chemically. Hereby the magnesium halide, the electron donor and the transition metal compound are, often in a solution, reacted with each other to form procatalyst compositions which can be easily separated.

In the US patent specifications 4,124,532 and 4,174,429 the preparation of this kind of catalytically active complexes by reacting in a suitable ratio the magnesium halide and the transition metal compound in an electron donor solution is described. The finished complex can be separated by evaporation crystallization of the solution mentioned or by precipitation of the complex with a solution in which it does not dissolve. As such complex compounds are produced as a result of a spontaneous crystallization they have a very regular crystal structure, which, simultaneously is disadvantageous for the polymerization.

In the US patent specification 4,302,566 and the EP application 6110 a precursor formed by magnesium halide, a transition metal compound and an electron donor is disclosed. The precursor is formed by precipitation from an electron donor solution, after which it is separated and agitated together with an aluminum alkyl, which activates it, and a separate inert carrier.

The US patent specification 3,989,881 discloses the polymerization of ethylene with a procatalyst prepared by precipitating from tetrahydrofuran solution together the tetrahydrofuran complex of magnesium dichloride and the tetrahydrofuran complex of titanium trichloride.

(Co)polymerization of ethylene in a gas phase by means of highly active catalysts is known through the US patent specifications 4,482,687; 4,383,095; 4,354,009; 4,349,648 and 4,359,561 and from EP publications 120503, 91135, 80052, 43220 and 20818. These catalysts are prepared from an organic aluminium compound and a precursor. Precursors have been used for the impregnation of porous inert carriers, such as silicon dioxide. A typical precursor composition is:



in which R is an aliphatic or aromatic hydrocarbon group having 1 to 14 carbon atoms or a group COR', in which R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms, X is Cl, Br and/or I and ED is an organic electron donor compound, such as an alkyl ester of an aliphatic or aromatic acid, an aliphatic ether, a cyclic ether or an aliphatic ketone. It should be noted that the precursor according to the formula is not formed of titanium alkyls $Ti(R)_n$, or alkyl halides $Ti(R)_nX_p$, but of titanium alkoxy halides $Ti(OR)_nX_p$.

On the other hand, various titanium compounds have been experimented for the improvement of the Ziegler-Natta-catalyst system. Thus, bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) has been used for the preparation of homogeneous polymerization catalysts.

In the US patent specification 3 161 629 the use of a non-supported monocyclopentadienyltitanium trichloride together with a triethylaluminium cocatalyst for the polymerization of ethylene is described. In addition to the fact that no carrier was used in that publication, neither the activity of the catalyst nor the properties of the polymer are given.

The present invention is concerned with the provision of a procatalyst consisting of a titanium compound, a magnesium compound and an electron donor having as amorphous a structure as possible and being thus as active as possible. Further, the invention is concerned with a procatalyst having a polymerisation lifetime as long as possible. The invention is also concerned with a method for the preparation of a solid procatalyst of an olefin polymerization catalyst system, which takes place without a separate grinding step of the magnesium halide, and with a use for the new procatalyst composition in the polymerization or copolymerization of olefins. The present invention therefore provides olefin polymerization catalyst system, a method for preparing the procatalyst thereof and a process for polymerizing olefins involving the use of the olefin polymerisation catalyst system.

The invention is based on the realization that the alteration of the morphology of a magnesium halide, being a condition of its activity, may be achieved by impregnating an inert carrier with a suitable electron donor solution comprising a magnesium halide. Another realization essentially connected with the invention is that by choosing a suitable titanium compound, i.e. monocyclopentadienyl titanium trichloride, a more active procatalyst having a more usable effective time is obtained.

The copolymerisation catalyst system according to the present invention comprises a procatalyst and a cocatalyst. The procatalyst comprises a solid carrier and a layer on its surface comprising a titanium compound, a magnesium compound and an electron donor. The titanium compound is monocyclopentadienyl titanium trichloride. The magnesium compound is a magnesium halide, and the electron donor is an alkyl ester of an aliphatic or aromatic carboxylic acid, an aliphatic ether, a cyclic ether or an aliphatic ketone.

The solid carrier can be any organic or inorganic substance which can be impregnated with the electron donor solution comprising the titanium compound and the magnesium compound and which does not disturb the activation of the transition metal compound. Suitable organic carriers include polymers and suitable inorganic carriers include e.g. silicon dioxide, aluminium oxide, magnesium oxide, magnesium silicate, and titanium oxide. Particularly advantageous carriers are silicon dioxide, aluminium oxide and magnesium silicate or mixtures thereof. The most advantageous is silicon dioxide.

It is preferable to heat the last-mentioned inorganic carriers to a temperature of 200 to 1000 °C to remove the water contained therein. If there are hydroxyl groups on the surface of the original carrier, it is, furthermore, preferable to treat the carrier chemically e.g. with aluminium alkyl or derivatives thereof, zinc alkyl, e.g. ZnR_2 , an organosilicon compound, a phosphorus compound or a fluorine compound. This is to remove surface hydroxy groups. Typical aluminium alkyl compounds include AlR_3 , AlR_2X , $\text{Al}(\text{i-Bu})_3$, $\text{Al}(\text{i-Bu})_2\text{H}$, in which R is an alkyl group and X is a halogen. Suitable organosilicon compounds include $(\text{R}_3\text{Si})_2\text{NH}$ and $\text{R}_n\text{SiX}_{4-n}$; suitable phosphorus compounds are PX_3 , POX_3 , $\text{P}(\text{OR})_3$, R_2PX , RPX_2 , and $(\text{R}_2\text{N})_2\text{POX}$ and suitable fluorine compounds are F_2 , HF , BF_3 , SiF_4 , SOF_2 .

The magnesium compound used in the invention is a magnesium halide, in which the halide is preferably chloride, bromide, iodide or a mixture thereof. The most preferable magnesium halide is anhydrous and dry magnesium dichloride, MgCl_2 .

In accordance with the invention the electron donor has monocyclopentadienyl titaniumtrichloride and the magnesium halide such as magnesium dichloride dissolved in it. Moreover, the electron donor must act as a modifier of the active centers and the morphology of the catalyst so that the activity and the lifetime of the catalyst are improved. Such electron donors are the alkyl esters of aliphatic or aromatic carboxylic acids, aliphatic ethers, cyclic ethers, or aliphatic ketones. The electron donor can be used either alone or as a combination of several electron donors.

As a cocatalyst of the catalyst system according to the invention can be used an organometallic compound of a metal of any of the groups IA to IIIA of the periodic table, such as trialkylaluminium or alkylaluminium halide or alkylaluminium sesquihalide. Particularly preferable are trialkylaluminium and alkylaluminium halides.

The present invention also relates to a method for the preparation of a solid procatalyst of an olefin polymerization catalyst system, in which the solid carrier is impregnated with a solution that is obtainable by dissolving a magnesium compound and monocyclopentadienyl titaniumtrichloride in a compound having the properties of an electron donor.

In the method the carrier, such as silicon dioxide, aluminium oxide or magnesium silicate, is first dehydrated preferably by heating it to a temperature of 200 to 1000 °C. Thereafter it can, if necessary, be treated with aluminium alkyl, zinc alkyl, organosilicon, phosphorus or fluorine compounds of the above-mentioned type for the removal of the surface hydroxyl groups. This chemical treatment takes place preferably by suspending the solid carrier into hydrocarbon and by adding the treating chemical mentioned to the suspension. After the treatment the suspension is dried to powder.

Such a calcination and/or chemical treatment of a carrier can be carried out for any of the various carriers mentioned, but it is particularly suitable for the pretreatment of silicon dioxide. Such a pretreated carrier can thereafter be treated with a suitable procatalyst precursor.

The precursor is prepared by dissolving monocyclopentadienyl titaniumtrichloride and a magnesium compound such as a magnesium halide into an electron donor compound of the above-mentioned type. The dissolving takes place at need by agitation at a temperature which is between 20 °C and the boiling point of the electron donor compound.

The monocyclopentadienyl titanium trichloride can be added to the electron donor compound either before the magnesium compound, simultaneously with it or after it.

Then the carrier is impregnated with the precursor solution. The carrier is added to the impregnation solution preferably in the form of a dry powder. The particle size of the powder is preferably 20 to 100 µm and it is preferably selected so that the particle size distribution is as narrow as possible. After the impregnation, which, at need, is carried out at elevated temperature, the electron donor surplus is removed e.g. by evaporation at a temperature between 20 to 150 °C.

The procatalyst of the obtained olefin polymerization catalyst system preferably has the following molar ratios: Ti/Mg = 0.1 to 1.0; Cl/Mg = 2.5 to 6 and electron donor (calculated as tetrahydrofuran)/Mg = 0.5 to 4.5.

In the experiments carried out in connection with the invention it was, surprisingly, noted that the performance capacity and the lifetime of the catalyst prepared in the above-described manner were excellent and that it was particularly suitable for the polymerization of olefins such as ethylene with high activity and good hydrogen and comonomer sensitivity.

Finally, the invention relates to the use of a polymerization catalyst system having a procatalyst of the above-mentioned type for the (co)polymerization of olefins, particularly ethylene.

The cocatalyst used with the procatalyst is an organometallic compound of a metal belonging to any of the groups IA to IIIA of the periodic table of elements, preferably an organoaluminium compound. Hereby, a separate preactivation can be carried out for the procatalyst with such an organic aluminium compound before it is added to the polymerization reactor and finally activated. Suitable preactivation substances are e.g. organoaluminium compounds having the formula AlR_3 , AlR_2X , AlR_3X_3 and Al_2R_4O , in which R is an alkyl and X a halogen.

The final activation preferably takes place in a reactor so that the total molar ratio of aluminium and titanium is equivalent to or greater than 20. The activation of a procatalyst can take place either in one or two stages.

The new Ziegler-Natta-catalyst according to the invention differs as to its properties from the prior art Ziegler-Natta-catalysts mainly in that it has a longer lifetime in the polymerization reactor and at least as good an activity, comonomer susceptibility, and morphology and at least as narrow a molecular weight distribution. The polymers obtained thereby have a wider melt index range (with the catalyst according to the invention the melt index values rise more when the hydrogen partial pressure is increased). Moreover, the monocyclopentadienyl titanium trichloride used in the new catalyst system is more stable and less toxic and corrosive than the titanium tetrachloride according to the prior art.

The preparation and comparison examples disclosed in the following will further illustrate the invention.

The preparation of the catalyst

Example 1

A. Treatment of the carrier with alkylaluminium

6.0g of silicon dioxide, the Davison degree of which was 955 and which had been dehydrated at 600 °C, was suspended into 36ml of pentane. The suspension was agitated and to it was added 5.13ml of 10% by weight pentane solution of triethylaluminium. The mixture obtained was agitated for 15 minutes and dried in nitrogen flow at room temperature for 2 hours, whereby dry, freely flowing powder containing 5.5% by weight of alkylaluminium, was formed.

B. Preparation of the precursor

To a 250ml flask furnished with a reflux cooler and a mechanical mixer was fed 500mg of anhydrous magnesiumdichloride, 384mg of monocyclopentadienyl titanium trichloride and 30ml of tetrahydrofurane.
 5 The mixture was held at 60 °C for 30 minutes for a complete dissolution of the substance.

C. Impregnation of silicon dioxide with the precursor

A homogeneous precursor solution was transferred by siphoning on silicon dioxide treated with
 10 aluminium alkyl. The suspension obtained was agitated for 15 minutes and dried at 85 °C (temperature of the bath) in a nitrogen flow for 4 hours.

The composition of the catalyst was: Mg 1.45%, Ti 0.97%, Al 1.03%, Cl 6.2%, THF 6.3%.

Example 2

15 The procedure was as in example 1, except that the catalyst was dried at 140 °C (temperature of the bath) for 2.5 hours.

The composition of the catalyst was: Mg 1.6%, Ti 0.89%, Al 1.91%, Cl 6.2%, THF 4.9%.

20 Example 3

The procedure was as in example 1, except that the dehydrated silicon dioxide was treated with 9.34ml of 10% by weight pentane solution of triethylaluminium for obtaining a carrier powder containing 10% by weight of alkyl aluminium.

25 The composition of the catalyst was: Mg 1.6%, Ti 0.87%, Al 2.0%, Cl 8.6%, THF 6.4%.

Example 4

30 The procedure was as in example 2, except that the dehydrated silicon dioxide was treated with 9.34ml of 10% by weight pentane solution of triethylaluminium for obtaining a carrier powder containing 10% by weight of alkyl aluminium.

The composition of the catalyst was: Mg 1.5%, Ti 0.9%, Al 1.9%, Cl 6.1%, THF 3.2%.

The comparison catalyst

35 The comparison catalyst was prepared in the same manner as the catalyst in Example 1. The only difference was that instead of monocyclopentadienyl titaniumtrichloride titanium tetrachloride (0.19ml) was used.

The composition of the catalyst was: Mg 1.3%, Ti 0.93%, Al 1.1%, Cl 7.7%, THF 6.5%.

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Preactivation with cocatalyst

All the catalysts according to the examples 1 to 4 and the comparison example were preactivated in the following manner:

45 0.5 to 2g of procatalyst was suspended in 3ml of pentane and mixed as 10% by weight pentane solution of alkyl aluminium was added to it. The molar ratio of the aluminium compound and the tetrahydrofurane was in the catalyst 0.8 to 1.2. The mixture was agitated at room temperature in nitrogen flow for about 20 minutes. The temperature of the bath was raised to 40 °C and the procatalyst was dried for one hour.

50 Polymerization

1. Experimental polymerization of ethylene

55 To a 3 liter reactor was added 2.1 liter of n-pentane dried with aluminium oxide and molecule sieves. Then 200mg of procatalyst suspended into a small amount of pentane was added through a feeding funnel to the reactor and the temperature was raised to 80 °C.

A 0.5 liter vessel was pressurized with hydrogen to a pressure of 5 bars. This hydrogen amount was fed together with the 10% by weight pentane solution of triethylaluminium acting as a cocatalyst and the

ethylene gas acting as the monomer into the reactor. The total pressure was raised by means of ethylene to 15 bars, the temperature was raised to 90 °C and the polymerization was continued for 60 to 90 minutes. Ethylene was continuously fed into the reactor to keep the pressure constant.

5 2. Copolymerization

The copolymerization of ethylene and alpha-olefins was carried out in the same manner as the polymerization, except that the comonomer (300ml of 4-methyl-1-pentene) was added into the medium (1800ml of n-pentane) immediately after the addition of the catalyst suspension.

10 The polymerization results obtained with the catalyst systems prepared according to the examples 1 to 4 and the comparison example have been presented in the table.

3. Experiments for the determination of the age of the catalyst

15 A procatalyst (= catalyst 1) preactivated with diethylaluminium chloride cocatalyst (Al/THF = 0.8) prepared according to example 1 and the comparison procatalyst were tested with ethylene, whereby 30mg of procatalyst and 2ml of 10% by weight pentane solution of triethylaluminium as the main cocatalyst was used. The polymerizations were carried out as described above, except that the polymerizations were allowed to go on for a longer time.

20 On the catalyst 1 polymerization of ethylene was continued for 6.5 hours. Hereby the yield of the polyethylene was 290g. The consumption of ethylene gas remained constant throughout the whole polymerization time. In the case of the comparison catalyst the consumption of ethylene decreased as a function of the polymerization time and the catalyst remained active only for 4.4 hours. The yield of the polyethylene was 176g.

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Table	Example 1		Examp. 2		Examp. 3		Examp. 4		Comparison
	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)	
Al-alkyl content of silicon dioxide	5.5 %	5.5 %	5.5 %	5.5 %	10 %	10 %	10 %	5.5 %	5.5 %
Drying temperature of catalyst (bath)	85°C	85°C	85°C	140°C	85°C	140°C	140°C	85°C	85°C
Preactivation substance Al/THF mol/mol	DEAC	DEAC	DEAC	DEAC	DEAC	DEAC	DEAC	DEAC	DEAC
Activation substance	0.8	0.8	1.2	0.8	0.8	0.8	0.8	0.8	0.8
Total-Al/Ti mol/mol	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA
Catalyst g	84	84	72	89	74	61	75	75	75
Polymerization time hours	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
H2-pressure 0.5 liter vessel, bar	1.5	1.5	1.0	1.5	1.5	1.5	1.5	1.5	1.5
PE g	5 bar	5 bar	5 bar	5 bar	5 bar	5 bar	5 bar	5 bar	10 bar
Activity kg PE/g Ti	554	213	330	427	193	245	538	312	312
Bulk density kg/m ³	322	124	165	267	134	102	274	159	159
MI(21.6)	320	310	340	330	350	320	350	320	320
MI(2.16)	8.1	148.9	12.8	11.6	8.9	3.7	17.7	90.2	90.2
Melt flow ratio	0.3	4.89	0.46	0.40	0.32	0.14	0.65	3.38	3.38
Mw	27.24	30.4	27.76	29.0	27.78	26.5	27.08	26.73	26.73
Mw/Mn	226 000	96 900	194 000	186 500	218 500	314 500			
Density g/cm ³	5.0	5.0	4.9	4.4	3.95	5.3			
	0.960		0.958	0.947			0.958		

The total pressure of the 3 liter reactor is 15 bars, DEAC = diethylaluminum chloride, TEA = triethylaluminum chloride

(*) Copolymerization with 4-methyl-1-pentene

Claims

1. An olefin polymerization catalyst system, the procatalyst of which comprises a solid inert carrier and on its surface a layer comprising a titanium compound and a magnesium compound in solution in an

electron donor, characterized in that the titanium compound is monocyclopentadienyl titanium trichloride, the magnesium compound is a magnesium halide, and the electron donor is an alkyl ester of an aliphatic or aromatic carboxylic acid, an aliphatic ether, a cyclic ether or an aliphatic ketone.

- 5 2. An olefin polymerization catalyst system according to Claim 1, wherein the solid carrier comprises silicon dioxide, aluminium oxide or magnesium silicate.
3. An olefin polymerization catalyst system according to Claim 1 or 2, characterized in that the procatalyst comprises, as the magnesium compound, magnesium chloride.
- 10 4. An olefin polymerization catalyst system according to any one of the preceding claims, characterized in that the molar ratios of the procatalyst are as follows: $Ti/Mg = 0.1$ to 1.0 ; $Cl/Mg = 2.5$ to 6 and the electron donor (calculated as tetrahydrofuran)/ $Mg = 0.5$ to 4.5 .
- 15 5. An olefin polymerization catalyst system according to any one of the preceding Claims, characterized in that it comprises a cocatalyst based on an organometallic compound of a metal belonging to any of the groups IA to IIIA of the periodic table of elements, and preferably based on trialkylaluminium.
- 20 6. A method for the preparation of a solid procatalyst of an olefin polymerization catalyst system, characterized by impregnating a solid inert carrier, with a solution obtainable by dissolving a magnesium halide and monocyclopentadienyl titanium trichloride in an electron donor which is an alkyl ester of an aliphatic or aromatic carboxylic acid, an aliphatic ether, a cyclic ether or an aliphatic ketone.
- 25 7. A method according to Claim 6, characterized by first treating the solid carrier by heating it to a temperature of from 200 to $1000^{\circ}C$ and/or by treating it chemically with aluminium alkyl or a derivative thereof, a zinc alkyl, an organosilicon compound, a phosphorus compound or a fluorine compound.
8. A method according to Claim 7, characterized by treating the solid carrier chemically by suspending it in a hydrocarbon and adding to the suspension a pretreatment chemical.
- 30 9. A method according to any one of Claims 6 to 8, characterized in that the procatalyst is as defined in any one of claim 1 to 4.
- 35 10. A process for polymerizing olefins characterized in that the polymerization is carried out in the presence of a polymerization catalyst system as claimed in any of claims 1 to 4 which further comprises, as cocatalyst, an organometallic compound of a metal belonging to any of the groups IA to IIIA of the periodic table of elements.
- 40 11. A process according to Claim 10, which further comprises, in addition to the normal activation of the procatalyst which takes place on the cocatalyst, preactivating the procatalyst in a separate stage with a cocatalyst of either the same type or of different type prior to polymerization.

Patentansprüche

- 45 1. Olefinpolymerisations-Katalysatorsystem, dessen Prokatalysator einen festen inerten Träger und auf dessen Oberfläche eine Schicht umfaßt, die eine Titanverbindung und eine Magnesiumverbindung in Lösung in einem Elektronendonator umfaßt, dadurch gekennzeichnet, daß es sich bei der Titanverbindung um Monocyclopentadienyltitantrichlorid handelt, es sich bei der Magnesiumverbindung um ein Magnesiumhalogenid handelt und es sich bei dem Elektronendonator um einen Alkylester einer aliphatischen oder aromatischen Carbonsäure, einen aliphatischen Ether, einen cyclischen Ether oder ein aliphatisches Keton handelt.
- 50 2. Olefinpolymerisations-Katalysatorsystem nach Anspruch 1, wobei der feste Träger Siliciumdioxid, Aluminiumoxid oder Magnesiumsilicat umfaßt.
- 55 3. Olefinpolymerisations-Katalysatorsystem nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Prokatalysator als Magnesiumverbindung Magnesiumchlorid umfaßt.

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4. Olefinpolymerisations-Katalysatorsystem nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die molaren Verhältnisse des Prokatalysators folgende Werte aufweisen: $Ti/Mg = 0,1$ bis $1,0$; $Cl/Mg = 2,5$ bis 6 und Elektronendonator (berechnet als Tetrahydrofuran)/ $Mg = 0,5$ bis $4,5$.
5. Olefinpolymerisations-Katalysatorsystem nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß es einen Cokatalysator auf der Basis einer organometallischen Verbindung eines Metalls, das zu einer beliebigen der Gruppen IA bis IIIA des Periodensystems der Elemente gehört, und vorzugsweise auf der Basis von Trialkylaluminium umfaßt.
6. Verfahren zur Herstellung eines festen Prokatalysators für ein Olefinpolymerisations-Katalysatorsystem, gekennzeichnet durch das Imprägnieren eines festen inerten Trägers mit einer Lösung, die durch Lösen eines Magnesiumhalogenids und von Monocyclopentadienyltitantrichlorid in einem Elektronendonator erhalten werden kann, bei dem es sich um einen Alkylester einer aliphatischen oder aromatischen Carbonsäure, einen aliphatischen Ether, einen cyclischen Ether oder ein aliphatisches Keton handelt.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß der feste Träger zuerst durch Erwärmen auf eine Temperatur von 200 bis $1000^{\circ}C$ und/oder chemisch mit einem Aluminiumalkyl oder einem Derivat davon, einem Zinkalkyl, einer Organosiliciumverbindung, einer Phosphorverbindung oder einer Fluorverbindung behandelt wird.
8. Verfahren nach Anspruch 7, gekennzeichnet durch die chemische Behandlung des festen Trägers durch Suspendieren in einem Kohlenwasserstoff und Zugabe einer Vorbehandlungschemikalie zu der Suspension.
9. Verfahren nach einem der Ansprüche 6 bis 8, dadurch gekennzeichnet, daß der Prokatalysator wie in einem der Ansprüche 1 bis 4 definiert ist.
10. Verfahren zur Polymerisation von Olefinen, dadurch gekennzeichnet, daß die Polymerisation in Gegenwart eines Polymerisations-Katalysatorsystems, wie es in einem der Ansprüche 1 bis 4 beansprucht wird, das ferner als Cokatalysator eine organometallische Verbindung eines Metalls, das zu einer beliebigen der Gruppen IA bis IIIA des Periodensystems der Elemente gehört, durchgeführt wird.
11. Verfahren nach Anspruch 10, das ferner zusätzlich zur normalen Aktivierung des Prokatalysators, die auf dem Cokatalysator stattfindet, eine Voraktivierung des Prokatalysators in einer getrennten Stufe mit einem Cokatalysator entweder des gleichen Typs oder eines anderen Typs vor der Polymerisation umfaßt.

Revendications

1. Système catalytique pour la polymérisation d'oléfines, dont le procatalyseur comprend un support inerte solide et sur la surface de celui-ci une couche comprenant un composé du titane et un composé du magnésium en solution dans un électro-donneur, caractérisé en ce que le composé du titane est du trichlorure de monocyclopentadiényl titane, le composé du magnésium est un halogénure de magnésium et l'électro-donneur est un ester alkylique d'un acide carboxylique aliphatique ou aromatique, un éther aliphatique, un éther cyclique ou une cétone aliphatique.
2. Système catalytique pour la polymérisation d'oléfines suivant la revendication 1, dans lequel le support solide comprend du dioxyde de silicium, de l'oxyde d'aluminium ou un silicate de magnésium.
3. Système catalytique pour la polymérisation d'oléfines suivant les revendications 1 ou 2, caractérisé en ce que le procatalyseur comprend du chlorure de magnésium en tant que composé du magnésium.
4. Système catalytique pour la polymérisation d'oléfines suivant l'une quelconque des revendications précédentes, caractérisé en ce que les rapports molaires du procatalyseur sont les suivants: $Ti/Mg = 0,1$ à $1,0$; $Cl/Mg = 2,5$ à 6 et électro-donneur (calculé en tant que tétrahydrofurane) / $Mg = 0,5$ à $4,5$.
5. Système catalytique pour la polymérisation d'oléfines suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'il comprend un co-catalyseur à base de composé organométallique

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d'un métal appartenant à l'un quelconque des groupes IA à IIIA du tableau périodique des éléments, et de préférence à base de trialkylaluminium.

- 5 6. Procédé pour la préparation d'un procatalyseur solide pour la polymérisation d'oléfines, caractérisé par l'imprégnation d'un support inerte solide avec une solution pouvant être obtenue par dissolution d'un halogénure de magnésium et de trichlorure de monocyclopentadiényl titane dans un électro-donneur qui est un ester alkylé d'un acide carboxylique aliphatique ou aromatique, un éther aliphatique, un éther cyclique ou une cétone aliphatique.
- 10 7. Procédé suivant la revendication 6, caractérisé par un traitement préalable du support solide par chauffage de celui-ci à une température comprise entre 200 °C et 1000 °C et/ou par traitement de celui-ci par voie chimique avec un alkylaluminium ou un dérivé de celui-ci, un zinc alkyle, un composé organosilicique, un composé du phosphore ou un composé du fluor.
- 15 8. Procédé suivant la revendication 7, caractérisé par le traitement du support solide par voie chimique par mise en suspension de celui-ci dans un hydrocarbure et addition à la suspension d'un agent chimique de pré-traitement.
- 20 9. Procédé suivant l'une quelconque des revendications 6 à 8, caractérisé en ce que le procatalyseur est tel que défini dans l'une quelconque des revendications 1 à 4.
- 25 10. Procédé pour la polymérisation d'oléfines, caractérisé en ce que la polymérisation est conduite en présence d'un système catalytique de polymérisation suivant l'une quelconque des revendications 1 à 4, qui comprend de plus, en tant que cocatalyseur, un composé organométallique d'un métal appartenant à l'un quelconque des groupes IA à IIIA du tableau périodique des éléments.
- 30 11. Procédé suivant la revendication 10, qui comprend de plus, en plus de l'activation normale du procatalyseur qui a lieu sur le cocatalyseur, la préactivation du procatalyseur dans une étape séparée avec un cocatalyseur soit du même type, soit d'un type différent avant la polymérisation.

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